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CONDUCTION IN POLYDIACETYLENE BILAYERS.(U)

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TECHNICAL REPORT NO. 2

CONDUCTION IN POLYDIACETYLENE BILAYERS

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## CONDUCTION IN POLYDIACETYLENE BILAYERS

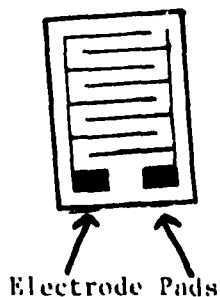
### INTRODUCTION

It has long been suspected that polydiacetylene single crystals should exhibit good semiconduction properties in view of the nature of the fully extended conjugated backbone. Experiments have shown however polydiacetylenes to be insulators<sup>(1a)</sup>. Doping of the polydiacetylene single crystals has resulted in a small increase in conductivity in some cases and in decomposition in others<sup>(1b)</sup>.

It is possible that only slight increases in conductivity (in comparison to polyacetylene) are observed because of low diffusion of the dopant to the inside of the polymer crystal. This has not been a problem with polyacetylene because of its sponge like morphology. Polymerized diacetylene monolayers are much better in this respect because of the high surface area and the very short path of diffusion for a dopant.

Conductivity of polymerized monolayers was measured by depositing them onto special 'lock and key'\* devices<sup>(2)</sup>. A lock and key device is equivalent to two long parallel electrodes but compacted into a small area (see below).

Lock and Key Schematic



(Lock and Key measures  
2.5 cm by 8.0 cm and has an  
effective parallel electrode  
length of 164 cm.)  
Electrode Separation = .015cm

\* We are grateful to Professor S.B.Senturia for supplying these devices.

This geometry allows conductivity to be measured within the monolayer plane.

### EXPERIMENTAL

Polydiacetylene monolayers were prepared by first forming a monomer monolayer on the surface of water and then polymerizing it with ultra violet irradiation under a nitrogen atmosphere (figure 1).<sup>(3)</sup> Conductivity measurements were performed on bilayers (two monolayers) made by dipping the lock and key device twice through a polymerized monolayer on the water surface. For these experiments,  $\text{CH}_3-(\text{CH}_2)_8\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-(\text{CH}_2)_8-\text{COOH}$  was used as the starting monomer. Lithium salts of this monomer were also formed by dissolving lithium hydroxide in the water substrate<sup>(3)</sup>.

A constant voltage of 60 volts DC was applied to the lock and key (with bilayer) and the resulting current was measured on a Kiethly 616 electrometer. Current values given in the following pages are absolute. In order to relate these values to a standard conductivity value, one has to assume either a bulk or surface conduction mechanism. If a bulk conduction is assumed, the standard conductivity can be arrived at by multiplying the given current values by a factor of 2.2. This arises from the cross sectional area of conduction and the conduction path length where:

$$\text{Conductivity} = I \cdot G \quad \text{where } I = \text{current measured}$$

$$G = \text{path length}$$

$$\text{voltage} \times \text{cross sectional area}$$

$$\text{For lock and key} \quad \text{path} = 150\mu = .015\text{cm}$$

$$\text{length} = 164\text{cm}$$

$$\text{Bilayer} \quad \text{height} = 70 \times 10^{-8} \text{cm}$$

$$G = 2.18$$

Because conduction was measured in only one direction within the bilayer plane and the crystallites were oriented randomly, nothing could be deduced about conduction anisotropy. If however all measured conduction is parallel to the polydiacetylene backbone and is negligible perpendicular to this direction, a higher conductivity would be implied along the polymer backbone than measured.

The ratio of the conductivity in a unidirectionally oriented bilayer to the actual randomly oriented bilayer can be calculated by integrating the vector components of the diacetylene backbones in a single chosen direction over the entire sample. This probably is not entirely correct but is sufficient to obtain a ball park estimate. From symmetry, the integration from 0 to  $\pi/2$  suffices and the ratio is:

$$\text{Ratio} = \frac{n}{\sum_0^{\pi/2} (\frac{\Delta\theta}{\pi/2} \times n) \cos \theta}$$

$$= \frac{\pi}{2 \int_0^{\pi/2} \cos \theta \, d\theta}$$

$$= \frac{\pi}{2 \int_0^{\pi/2} \sin \theta} = 1.57$$

$n$  = total number of vectors in an all parallel sample

$\frac{\Delta\theta \times n}{\pi/2}$  = fraction of vectors in a small slice  $\Delta\theta$  of a random sample

$\frac{\Delta\theta \times n}{\pi/2} \cos \theta$  = component of that fraction in a given direction

From this, the conductivity along the chain direction can be said to be a factor of 3.4 higher ( $2.18 \times 1.57$ ) than the current values given in the subsequent data if it is assumed that there is a bulk conduction mechanism and it occurs only in the chain direction. Even if these assumptions are not made, the changes in current that are measured are still directly proportional to conductivity changes. Absolute current values varied by as much as an order of magnitude from experiment to experiment depending on film perfection and probably other unknown factors, but the changes in current (or relative conductivity) remained fairly constant.

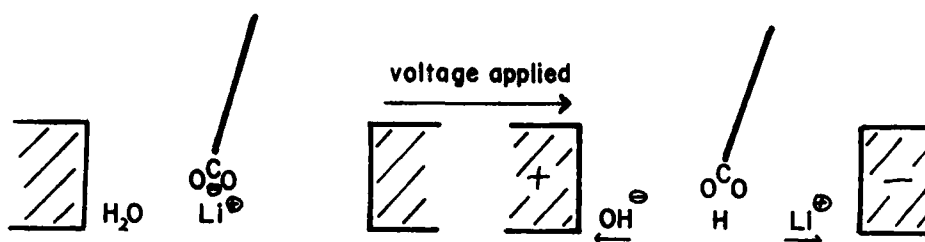
Both the free acid and Li-salt bilayers were doped in hopes of observing increases in conductivity. Of the many dopants commonly used with polyacetylene, iodine is the cheapest and safest, and was therefore used with the bilayers. The basic apparatus for doping is shown in figure 2. The process consists of passing dry nitrogen over crystalline iodine and then over the bilayer on the lock and key.

Before iodine was passed over the bilayer samples, clean nitrogen was first passed through the chambers to purge it and obtain a steady current reading. Initially large variations were obtained in the results until it was noticed there was a large dependence on ambient lighting conditions.

## RESULTS AND DISCUSSION

### 1. Lithium Salt Bilayer

Lithium salt bilayers (hydrophillic core) deposited on lock and key devices showed an initial current at 60 VDC of about  $10^{-7}$  amperes. After minutes this lowered to  $10^{-8}$  amps and after a period of days to approximately  $10^{-11}$  amps. This kind of behaviour is common to most polymers where space charges migrate to the poles under and electric field<sup>(4)</sup>. After a period of time, this decays and only the so called true current remains. If the voltage source is then shorted out, a current is observed in the opposite direction as the space charge flows back to the preferred "even" distribution, a behaviour similar to that of a storage battery. It follows then that the higher the ionic content of the polymer, the higher this initial conduction. In the case of the lithium salt bilayer the initial conduction is probably largely due to Li migration and has been found to be aided by trace amounts of water. If the initially formed Li salt bilayer is subject to a reduced pressure, the conductivity is observed to decrease (figure 3). The current at  $10^{-2}$  microns ( $10^{-5}$  torr) is on the order of  $10^{-11}$  amps or equivalent to the true current. As air is brought back in contact with the bilayer the current was observed to increase nearly back to the original value. Dry nitrogen passed over the sample also caused the current to drop to on the order of  $10^{-11}$  amps. Both these observations indicate that the presence of water aids somehow in the space charge migration process, possibly by the following scheme:



In order to eliminate effects of space charge currents, measurements on Li-salt bilayers were made after 60 VDC had been applied to the sample for three days. Any changes in current on a short time scale after this were assumed to be fluctuations in the true current.

## 2. Free Acid Bilayers

For polymerized free acid bilayers formed on the lock and key device, the initial current flow was measured at  $10^{-7}$  amps, similar to the Li-salt bilayer. The decay was much faster however and a "true" current value of  $10^{-11}$  amps was reached on the order of minutes after voltage application instead of days as is the case with the Li-salt bilayer. The much quicker leveling off in the free acid is in accordance with the fact that there are almost no ions present<sup>(4)</sup>. The initial space charge current that is observed is probably due to impurities in the water and possibly even aluminum from evaporated electrodes. The free acid bilayers also exhibited similar behavior to that of the Li-salt bilayer membranes under the influence of vacuum and dry nitrogen.

## 3. Doping and Photoconduction

The free acid bilayer exhibits an initial dark current of about  $10^{-11}$  amps as previously mentioned but as the iodine is introduced, a large increase in current is observed (figure 4). A maximum is reached after about 12 minutes at about  $3 \times 10^{-8}$  amps which is an increase of over three orders of magnitude.

Although this is a very large increase, the bilayer has in reality only changed from a good insulator to a poor one. When pure nitrogen is switched back into the bilayer chamber, the current decays back, almost to its original value. When the same experiment is run under illuminated conditions (75 watt light bulb one inch from bilayer) the result is very similar (heating from the light bulb was prevented by an intermediate glass barrier). A difference in the initial current is observed of about one order of magnitude due to a photoconductive effect. Upon doping, about the same maximum is reached and this also decays to the original value after the iodine is removed. Iodine content of the nitrogen and the flow rate were not monitored so the difference in rate of increase of the dark and illuminated samples in figure 4 cannot be compared and may be artifact.

In the case of the Li-salt bilayer, the dark current was initially about  $5 \times 10^{-11}$  amps and increased only slightly upon exposure to iodine to a value of  $1.3 \times 10^{-10}$ . Illuminated samples were observed to have a photoconductive increase of over an order of magnitude (figure 5). Upon doping the illuminated sample an increase in current was observed comparable to the free acid bilayer.

#### 4. Monomer Bilayers

Monomer bilayers were made and measured in the same way as the polymerized layers as a check for backbone participation in the conduction mechanism. Very similar space charge currents were observed for the monomer bilayers of both the free acid and Li-salt bilayers. Both types of bilayers however showed absolutely no response to illumination and almost none to doping. This indicates that the polymer backbone has little effect in the conduction mechanism of a dark undoped sample but only comes into play upon illumination or doping.



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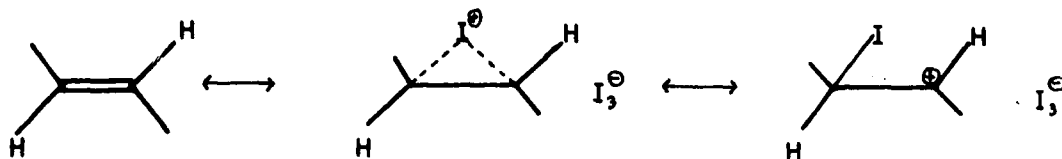
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## 5. Conduction Mechanism

Although the effect of a dopant in a conjugated system is not well understood, one possible mechanism that has been generally accepted is the association of the dopant directly with a double or triple bond. Depending on the dopant, it either acts to donate or withdraw electrons, creating an extra electron or a hole in the chain which can then migrate. For iodine in polyacetylene it has been suggested<sup>(5)</sup> that the following may occur:



Once the hole is formed then migration can occur:



If this were all that was occurring in the bilayer systems, no difference should be observed between the free acid and Li-salt bilayers. Quite a significant difference is exhibited however in the unilluminated doped free acid bilayer (high current flow) and the unilluminated doped Li-salt bilayer (low current flow). The conduction which is known to be occurring along the polymeric backbone (from lack of monomer response) is somehow effected by the hydrophilic portions of the bilayer. At the present time however, the cause of these phenomena are not well understood.

### Conclusion

↓  
Diacetylene monolayers polymerized at the gas water interface have a very poor conductivity. They do however exhibit a photoconductive and doping effect which can raise the conductivity over three orders of magnitude. Because of the initially low conductivity, the polydiacetylene monolayers could at best only be considered a poor semiconductor after doping. The possibility still remains that more exotic dopants such as  $\text{AsF}_5$  that are successfully applied to other conjugated polymers may result in higher conductivities in polydiacetylene monolayers.  
↑

### Acknowledgement

The support of the office of Naval Research under ONR Project N00014-77C-0213 is gratefully acknowledged.

## FIGURES

1. Polymerization reaction of diacetylene monolayers at the gas water interface.
2. Doping apparatus for diacetylene layers on a lock and key device.
3. Dependence of current on pressure. (Li salt bilayer)
4. Photoconductive and doping behaviour of free acid bilayer.  
(o = dark current, x = illuminated sample)
5. Photoconductive and doping behaviour of Li salt bilayer.  
(o = dark current, x = illuminated sample)

FIGURE 1

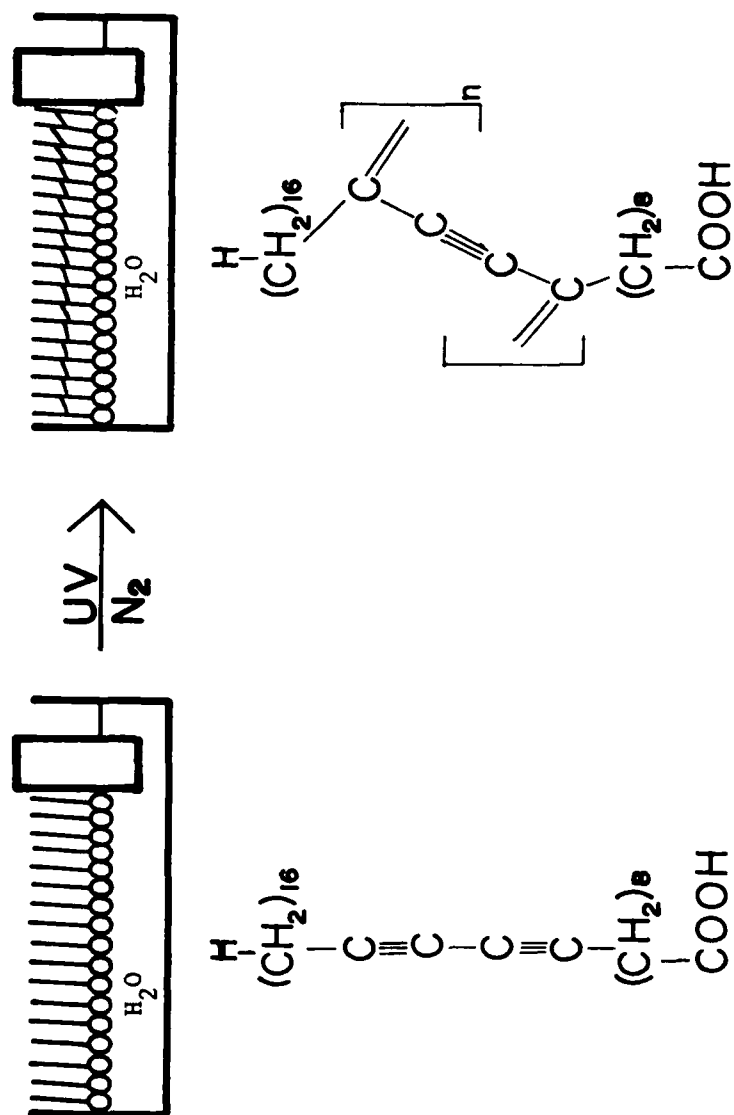


FIGURE 2

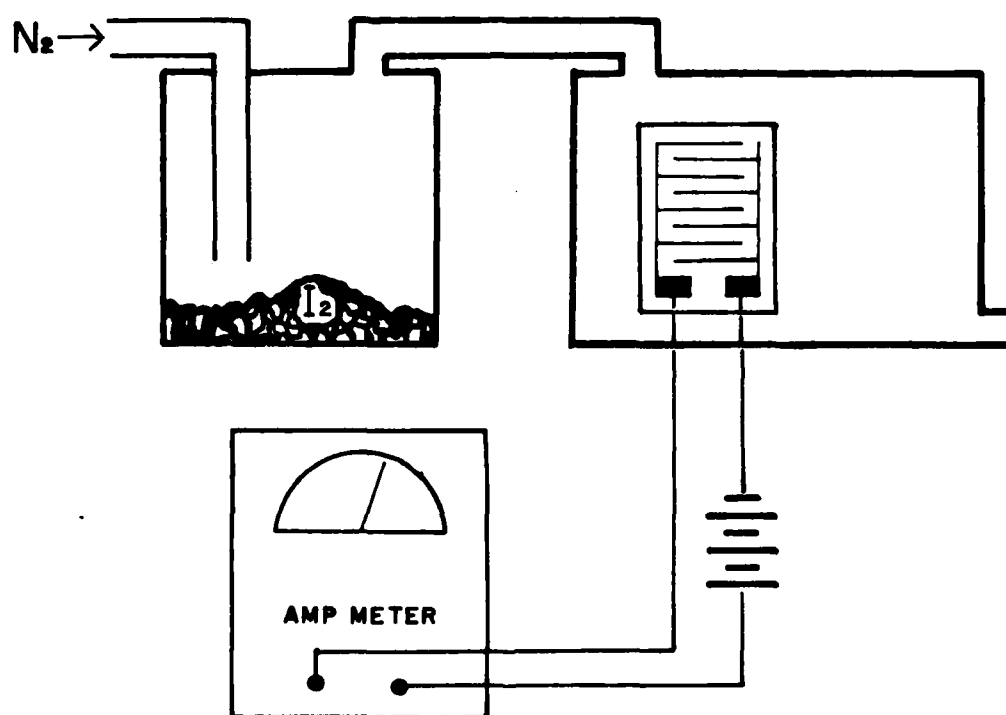


FIGURE 3

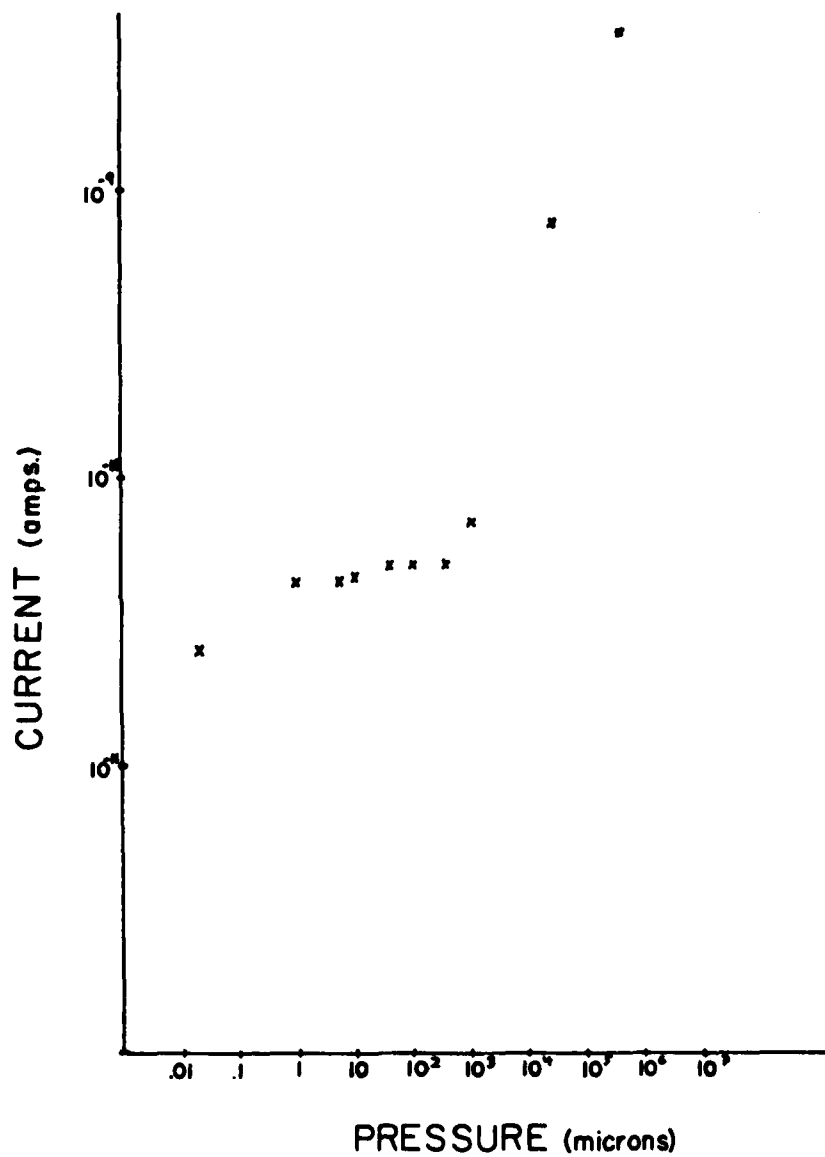


FIGURE 4

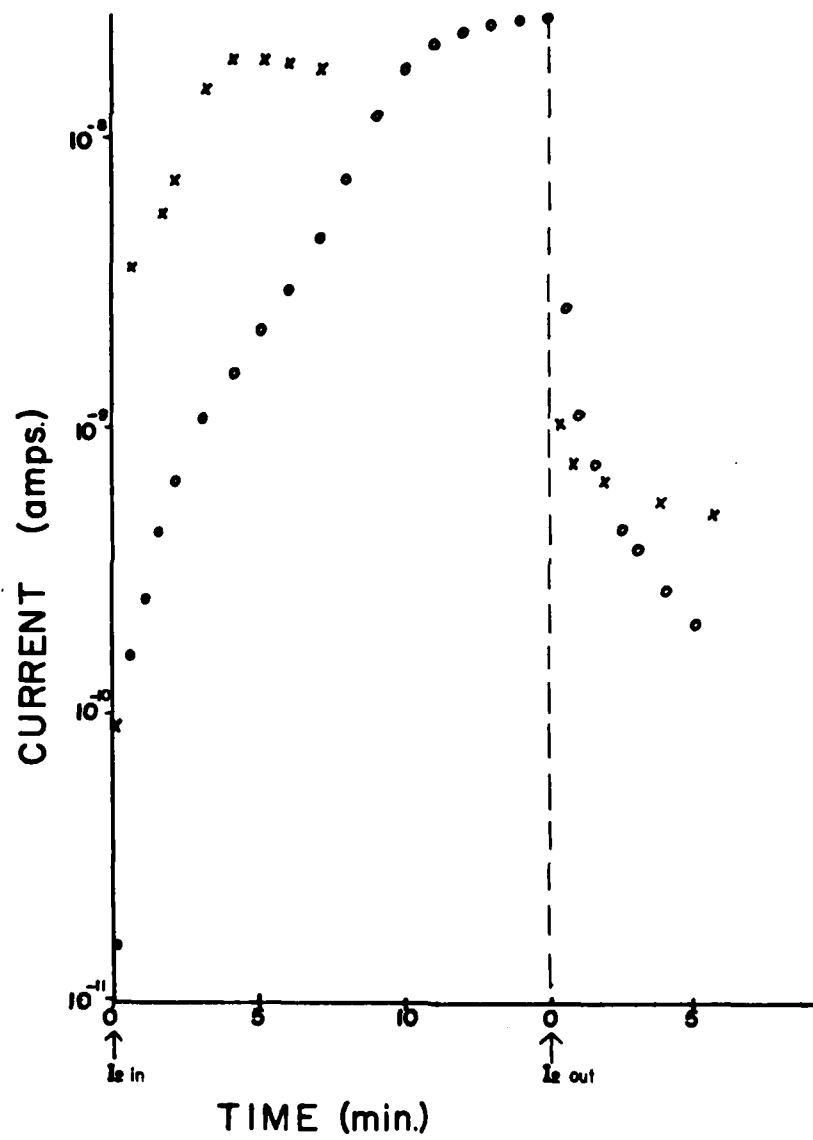
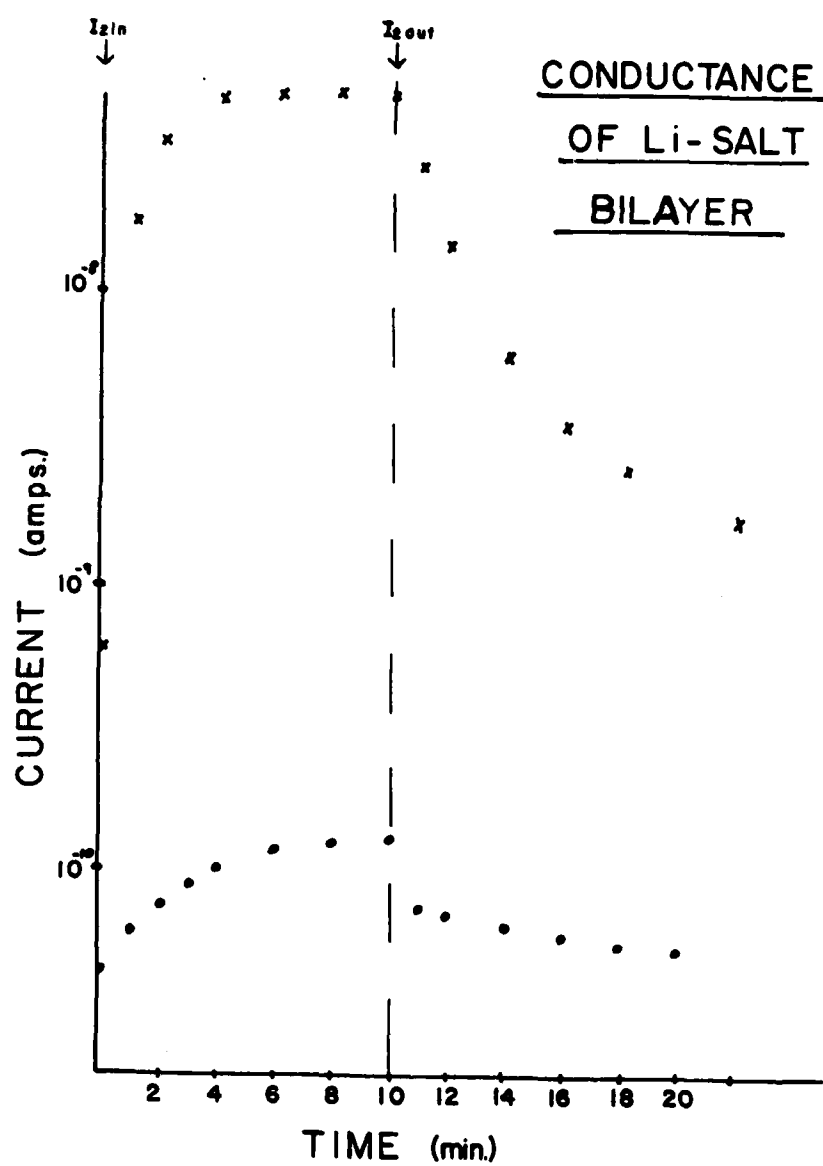




FIGURE 5



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